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Catalysis Today 82 (2003) 127–139

CATALYSIS TODAY

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Effect of incipient removal of hydrogen through palladium membrane on the conversion of methane steam reforming Experimental and modeling

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Abstract

This paper presents a mathematical model based on the reaction rate expressions to describe the displacement of methane conversion in the steam reforming. The effect of several parameters including weight hourly space velocity (WHSV), load-to-surface ratio, reaction pressure, hydrogen partial pressure in permeate side and reaction temperature were investigated. Simulation and experimental results showed that a conversion higher than 80% could be achieved in a palladium membrane reactor at reaction temperature of 500 °C relative to 850 °C in a conventional fixed bed reactor (FBR). Besides, the yield of CO (<2%) in membrane reactor was much lower than that (>50%) in the FBR, which indicated the significant depression of CO production in use of membrane reactor.

Keywords: Palladium membrane; Steam reforming; WHSV; Load-to-surface ratio

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1. Introduction

Hydrogen is conventionally produced on a large-scale by the steam reforming of hydrocarbons such as methane or naphtha oil. Due to the endothermic properties of steam reforming reactions, the conversion of reactant, e.g. methane, is usually restricted by the thermodynamic equilibrium [1,2]. In recent years, palladium-based membrane has been used to shift the thermodynamic equilibrium of methane steam reforming toward the product side at temperature as low as 500 °C. Obvious displacement of equilibrium conversion was readily reported by use of a membrane reactor [3–5]. Almost complete conversion of methane to hydrogen and carbon dioxide can be attained even at low temperatures. The produced hydrogen is free of CO and CO_2 so that it can be applied to a polymer or alkali electrolyte fuel cell operating at low temperatures [4,6].

Due to the continuous withdrawal of hydrogen from reaction system by Pd-based membrane, the displacement of equilibrium conversion of methane was experimentally demonstrated in several references. This enhancement is the so-called “drain-off” effect of hydrogen removal [3,7]. The simulation on the behavior of palladium membrane reactor used in methane steam reforming were also attempted to illustrate the enhancement of equilibrium conversion [1].

In a previous paper [8], we established a permeation model to describe the results of displacement of

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doi:10.1016/S0920-5861(03)00212-8

Nomenclature

F_i	flow rate of component i in the reaction side (kmol h^{-1})
$F_{H_2}^{p}$	flow rate of hydrogen in the permeate side (kmol h^{-1})
F_i^0	flow rate of component i in the entrance of reaction side (kmol h^{-1})
k_i	rate constant for reaction i; units will be specific to the form of the rate expression
K_i	equilibrium constant of reaction i or adsorption coefficient for component i
ℓ	distance from the inlet of membrane tube (m)
L	total length of membrane tube (m)
L/S	load-to-surface ratio, the ratio of inlet (volumetric) flow rate of methane relative to the surface area of the palladium membrane tube (m^3 h^{-1} m^{-2})
m	molar ratio of steam to methane in the feedstock (–)
$m_{H_2}^0$	molar ratio of hydrogen to methane in the feedstock (–)
P_i	partial pressure of component i in the reaction side (atm)
P_p	hydrogen partial pressure in the permeate side (atm)
P_r	total pressure in the reaction side (atm)
r_i	rate of reaction i (kmol h^{-1} kg^{-1})
R_m	radius of the membrane tube (m)
W	weight of catalyst (kg)
WHSV	the hourly weight of inlet methane relative to loaded catalyst weight (h^{-1})
X_i	conversion of component i or dimensionless flow rate of component i relative to initial flow rate of methane in reaction side (–)
Y_{H_2}	dimensionless flow rate of hydrogen relative to initial flow rate of methane in permeate side (–)
z	dimensionless distance from the inlet of the membrane tube (–)

Greek symbols

β	permeance of palladium membrane (m^3 m^{-2} h^{-1} atm$^{-0.5}$)
τ_r	reaction contact time, the ratio of catalyst weight relative to the inlet (molar) flow rate of methane, which is the reverse of WHSV as the flow rate of methane in weight (kg h kmol^{-1})
τ_m	parameter related membrane surface area with the inlet (molar) flow rate of methane, which is the reverse of load-to-surface ratio as the flow rate of methane in volume (m^2 h kmol^{-1})

Subscripts and superscripts

i	ith component or ith reaction
0	inlet condition

equilibrium conversion in a tubular palladium membrane reactor. Only the overall reaction of methane steam reforming was considered to simplify the analytical solution of the permeation model. In this paper, we further present a mathematical model, based on the rate expressions of three reversible reactions involved in methane steam reforming, to investigate the effect of hydrogen removal on the conversion of methane. The influence of two major operating parameters, i.e. weight hourly space velocity (WHSV) and load-to-surface ratio, on the conversion enhancement is also simulated. Experimental tests were conducted too, to examine the agreement with the calculated results.

2. Mathematical model

2.1. Basic assumptions

(1) Isothermal and isobaric reaction conditions;
(2) Steady-state operation;

(3) Plug flow on both reaction and permeation sides;
(4) Intrinsic kinetics for methane steam reforming and water gas shift reactions;
(5) No boundary layer on membrane surfaces.

2.2. Reaction rate expressions

Methane steam reforming involves two reversible reactions: the reforming (1) and water gas shift reaction (2). The overall reaction is expressed in (3).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^{\circ}_{298\,K} = +206\,kJ/mol \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298\,K} = -41\,kJ/mol \tag{2}$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta H^{\circ}_{298\,K} = +165\,kJ/mol \tag{3}$$

The rate expressions for reactions (1)–(3) are obtained from [1]. The unit of each reaction rate is expressed in $\mathrm{kmol\,h^{-1}\,kg^{-1}}$.

$$r_1 = \frac{k_1}{P_{H_2}^{2.5}} \frac{P_{CH_4}P_{H_2O} - (P_{H_2}^{3}P_{CO}/K_1)}{\mathrm{DEN}^2} \tag{4}$$

$$r_2 = \frac{k_2}{P_{H_2}} \frac{P_{CO}P_{H_2O} - (P_{H_2}P_{CO_2}/K_2)}{\mathrm{DEN}^2} \tag{5}$$

$$r_3 = \frac{k_3}{P_{H_2}^{3.5}} \frac{P_{CH_4}P_{H_2O}^{2} - (P_{H_2}^{4}P_{CO_2}/K_3)}{\mathrm{DEN}^2} \tag{6}$$

$$\mathrm{DEN} = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}}$$

with the partial pressure of each component given as:

$$P_{CH_4} = (1 - X_{CH_4})\sigma, \qquad P_{H_2O} = (m - X_{H_2O_2})\sigma,$$
$$P_{CO} = X_{CO}\sigma, \qquad P_{H_2} = (m_{H_2}^{0} + X_{H_2})\sigma,$$
$$P_{CO_2} = X_{CO_2}\sigma,$$
$$\sigma = \frac{P_r}{1 + m + m_{H_2}^{0} + X_{H_2} - X_{CH_4} - X_{H_2O} + X_{CO} + X_{CO_2}}$$

where P_r is the pressure in the reaction side of the reactor, m the steam to methane ratio and $m_{H_2}^{0}$ the hydrogen to methane ratio in the feedstock. The X_i and Y_i are defined as:

$$X_{CH_4} = 1 - \frac{F_{CH_4}}{F_{CH_4}^{0}}, \qquad X_{H_2O} = 1 - \frac{F_{H_2O}}{F_{CH_4}^{0}},$$
$$X_{CO} = \frac{F_{CO}}{F_{CH_4}^{0}}, \qquad X_{CO_2} = \frac{F_{CO_2}}{F_{CH_4}^{0}},$$
$$X_{H_2} = \frac{F_{H_2}}{F_{CH_4}^{0}}, \qquad Y_{H_2} = \frac{F_{H_2}^{p}}{F_{CH_4}^{0}}$$

The changing rate of each component along the reactor length were thus given as:

$$\frac{dX_{CH_4}}{dz} = \tau_r(r_1 + r_3) \tag{7}$$

$$\frac{dX_{CO_2}}{dz} = \tau_r(r_2 + r_3) \tag{8}$$

$$\frac{dX_{CO}}{dz} = \tau_r(r_1 - r_2) \tag{9}$$

$$\frac{dX_{H_2O}}{dz} = \tau_r(r_1 + r_2 + 2r_3) \tag{10}$$

$$\frac{dX_{H_2}}{dz} = \tau_r(3r_1 + r_2 + 4r_3) - \frac{dY_{H_2}}{dz} \tag{11}$$

and the permeation rate of hydrogen through palladium membrane was given as:

$$\frac{dY_{H_2}}{dz} = \tau_m\beta(P_{H_2}^{0.5} - P_{p}^{0.5}) \tag{12}$$

with $\tau_r = W/F_{CH_4}^{0}$ and $\tau_m = 2\pi R_m L/F_{CH_4}^{0}$, where W is the catalyst weight, F_i the flow rate of component i in reaction side, F_i^0 the flow rate of component i in the entrance of reaction side, P_p the partial pressure of hydrogen in the permeate side, R_m the radius of the membrane tube, L the total length of membrane tube, β the permeance of palladium membrane and $z = \ell/L$ the dimensionless length of the membrane tube. In experiments, two operation parameters WHSV and load-to-surface ratio are used instead of τ_r and τ_m. Theoretically, WHSV and load-to-surface ratio are the reverse of τ_r and τ_m, respectively.

In rate equations (4)–(6), a critical parameter is the hydrogen partial pressure, P_{H_2}. A hydrogen-free methane/steam feedstock ($m_{H_2}^{0} = 0$) will result in an infinite initial reaction rate because the inlet hydrogen partial pressure is zero. The problem can be

Table 1
Kinetic parameters used to calculate the conversion of methane

Parameter	Pre-exponential factor	E or ΔH (kJ/mol)
k_1 (kmol atm$^{0.5}$/kg h)	4.2248×10^{15}	240.1
k_2 (kmol/kg h atm)	1.955×10^{6}	67.13
k_3 (kmol atm$^{0.5}$/kg h)	1.0202×10^{15}	243.9
K_{CO} (atm^{-1})	8.23×10^{-5}	−70.65
K_{H_2} (atm^{-1})	6.12×10^{-9}	−82.9
K_{CH_4} (atm^{-1})	6.65×10^{-4}	−38.28
K_{H_2O} (–)	1.77×10^{5}	88.68

solved by setting a very small $m^0_{H_2}$. In the present study, $m^0_{H_2} = 1.0 \times 10^{-6}$ was preset. However, this value needs a small calculation step size for solving Eqs. (7)–(12) in order to get a sufficient accuracy. This means that it may cause a longer computation time. In order to compromise the accuracy and computation time, Eqs. (7)–(12) can be solved by an adaptive step size control method, i.e. Runge–Kutta–Fehlberg method [9].

The kinetic parameters obtained from [1] were used for the simulation. The equilibrium constants of reactions (1)–(3) were obtained from [2]. The permeance of supported Pd membrane was obtained in this work. The values of kinetic and equilibrium/permeation parameters are summarized in Tables 1 and 2, respectively.

2.3. Considerations in cases of “initial” and “ultimate” equilibrium

According to the reactions (1)–(3), the conversion of methane is mainly determined by the formation of CO_2 and CO. The sum of yields of CO_2 and CO should equal to the conversion of methane if no carbon deposition is present on the catalyst surface. At the status of equilibrium, only two independent reactions, i.e. reactions (1) and (3) were necessarily considered to calculate the equilibrium composition of CO and CO_2 based on the equilibrium constants of both reactions. Therefore, the conversion of methane could be obtained by summing up the yield of CO and CO_2. The equilibrium constants of reactions (1) and (3) could be, respectively, expressed as follows:

$$K_1 = \frac{P^3_{H_2} P_{CO}}{P_{CH_4} P_{H_2O}} \tag{13}$$

$$K_3 = \frac{P^4_{H_2} P_{CO_2}}{P_{CH_4} P^2_{H_2O}} \tag{14}$$

where

$$P_{CH_4} = \frac{1 - X_{CO} - X_{CO_2}}{D} P_r,$$

$$P_{H_2O} = \frac{m - X_{CO} - 2X_{CO_2}}{D} P_r, \qquad P_{CO} = \frac{X_{CO}}{D} P_r,$$

$$P_{CO_2} = \frac{X_{CO_2}}{D} P_r,$$

$$P_{H_2} = \frac{3X_{CO} + 4X_{CO_2} - Y_{H_2}}{D} P_r$$

with $D = 1+m+2X_{CO}+2X_{CO_2}-Y_{H_2}$. The conversion of methane $X_{CH_4} = X_{CO} + X_{CO_2}$.

There are two extreme cases that should be considered:

Case 1. In the “initial” stage, if $P_{H_2} \leq P_p$, then $Y_{H_2} = 0$, i.e. no hydrogen is removed through the membrane. Solving Eqs. (13) and (14) simultaneously, X_{CO} and X_{CO_2} could be obtained for the condition of initial equilibrium. We can thus obtain the initial equilibrium conversion of methane as $X_{CH_4} = X_{CO} + X_{CO_2}$, which is the same as the value achieved in the conventional fixed bed reactor (FBR), without the use of palladium membrane.

Case 2. In the “ultimate” stage, P_{H_2} is approaching to P_p due to continuous removal of hydrogen, and then $P_{H_2} = P_p$. Therefore, one additional equation could be established when combined with the expression of hydrogen partial pressure as follows:

Table 2
Equilibrium constants and permeance of Pd membrane used in simulation[a]

Parameter	Pre-exponential factor	E or ΔH (kJ/g mol)
K_1 (atm^2)	7.846×10^{12}	220.2
K_2 (–)	1.412×10^{-2}	−37.72
K_3 (atm^2)	1.11×10^{11}	182.4
β (m^3 m^{-2} h^{-1} atm$^{-0.5}$)[b]	56.41	12.54

[a] The equilibrium constants K_1–K_3 were calculated in temperature range 573–873 K from [2].

[b] The permeance β was measured in temperature range 593–773 K.

$$Pp = P_{H_2} = \frac{3X_{CO} + 4X_{CO_2} - Y_{H_2}}{D} P_r \quad (15)$$

Solving Eqs. (13)–(15) simultaneously, X_{CO}, X_{CO_2} and Y_{H_2} could be obtained for the status of ultimate equilibrium. The ultimate equilibrium conversion of methane is then calculated as $X_{CH_4} = X_{CO} + X_{CO_2}$, which is the highest conversion being enhanced under the effect of palladium membrane.

3. Experimental

The supported palladium membrane tube was prepared by the electroless plating technique described in [10]. A porous 316L stainless steel tube having an outside diameter of 1.27 cm was used as the support. The effective membrane area for hydrogen separation is around 60 cm^2. The thickness of palladium membrane is about 20 μm. The activation energy of measured permeance of the membrane is near 3 kcal/mol as shown in Table 2.

The steam reforming reaction was conducted in a single-jacketed membrane reactor which is simply constructed from a membrane tube with a stainless steel tube as outer jacket. The operating procedures were the same as that described in the previous work [6]. A nickel catalyst, C11-9-02 from Nissan Girdler Co., was used for methane steam reforming in temperature range 400–500 °C. The steam to methane ratio was 3. The reaction pressure used was in the range 9–20 atm. The permeate side of the membrane tube was operated under atmospheric pressure. In case of experiments without the use of sweeping gas, the partial pressure of hydrogen in the permeate side was accounted for 1 atm because almost 100% purity of hydrogen was obtained due to the high selectivity of palladium membrane. In case of the tests for hydrogen partial pressure below 1 atm, the nitrogen gas was used as sweeping gas to dilute the concentration of hydrogen permeated through the palladium membrane. The flow rate of nitrogen was in the range 100–500 ml/min and the resulting hydrogen partial pressure in permeate side was 0.2–0.7 atm. The simulated value of each component was solved numerically by a fourth-order Runge–Kutta method as described in Section 2.2. The results were calculated in both cases with and without sweeping gas for comparison to experimental data at hydrogen partial pressure of 1 atm or below in the permeate side.

4. Results and discussion

4.1. Effect of WHSV and load-to-surface ratio on the conversion of methane

Two major working parameters, WHSV of methane and load-to-surface ratio, were found to significantly affect the conversion of methane in the steam reforming reaction. The WHSV of methane is reported in terms of the hourly weight of inlet methane over loaded catalyst weight. The load-to-surface ratio is defined as the ratio of methane inlet flow rate relative to the surface area of the palladium membrane tube. The higher WHSV and load-to-surface ratio, the lower catalyst weight and membrane area, respectively.

The effect of WHSV on conversion of methane is shown in Fig. 1. The simulation results from the mathematical modeling obviously indicated that the methane conversion decreased with increasing WHSV. At reaction pressure of 9 atm and permeate hydrogen partial pressure of 1 atm, the conversion is lower than its initial equilibrium conversion (19%) when WHSV is greater than 100 h^{-1}. No more conversion was enhanced with increasing membrane area, due to the very low hydrogen produced and removed from the reaction system. When WHSV is below 3 h^{-1}, the conversion reaches its equilibrium status and cannot be enhanced by reducing the WHSV. In summary, for high WHSV (or low reaction contact time), the reaction system does not reach the thermodynamic equilibrium so that the conversion is lower than the thermodynamic one. For low WHSV (or high contact time) the reaction system is in equilibrium, so the enhancement of the conversion depends on the amount of hydrogen removed from the reactive medium. The amount of removed hydrogen is strongly influenced by the pressure difference across the membrane. As can be seen in Fig. 1, the conversion does not reach the maximum value (100%) for a large enough membrane area (low load-to-surface ratio) and for low WHSV because of inadequate removal of hydrogen as the pressure difference is not enough across the membrane.

The load-to-surface ratio also showed strong effect on the enhancement of the methane conversion.

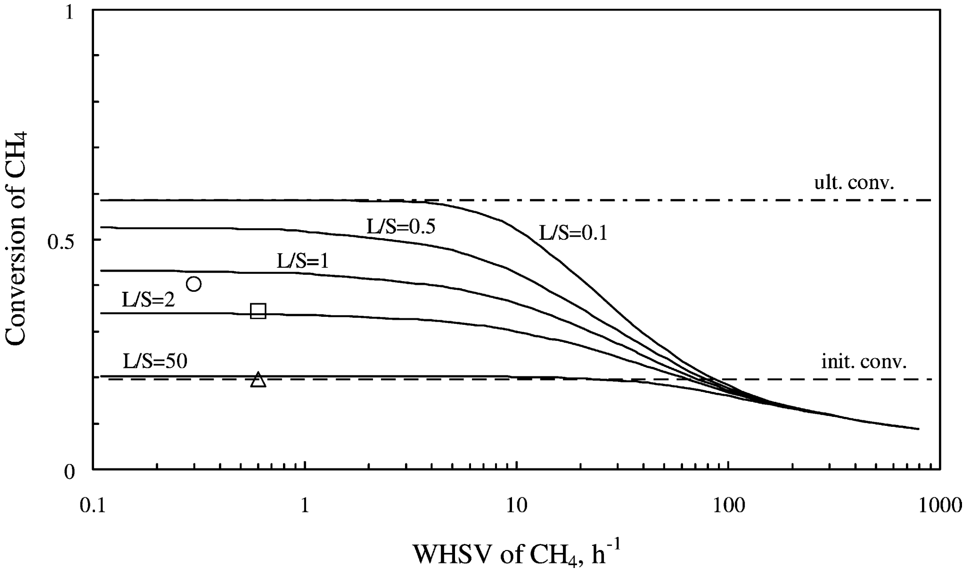

Fig. 1. Effect of WHSV on the conversion of methane at 500 °C, 9 atm and different load-to-surface ratio. The hydrogen partial pressure in permeate side was 1 atm. Experimental data were obtained at load-to-surface ratio = 1 $m^3/h\,m^2$ (○), 2 $m^3/h\,m^2$ (□) and in conventional FBR (△).

Decreasing the load-to-surface ratio significantly increases the conversion (Fig. 2). At WHSV $< 3\,h^{-1}$, the conversion approaches the ultimate equilibrium conversion of 58% as load-to-surface ratio is below 0.2 $m^3/h\,m^2$. On the other hand, the conversion will stay at the initial equilibrium conversion of 19% as load-to-surface ratio above 50 $m^3/h\,m^2$. This initial conversion is equivalent to the equilibrium conversion

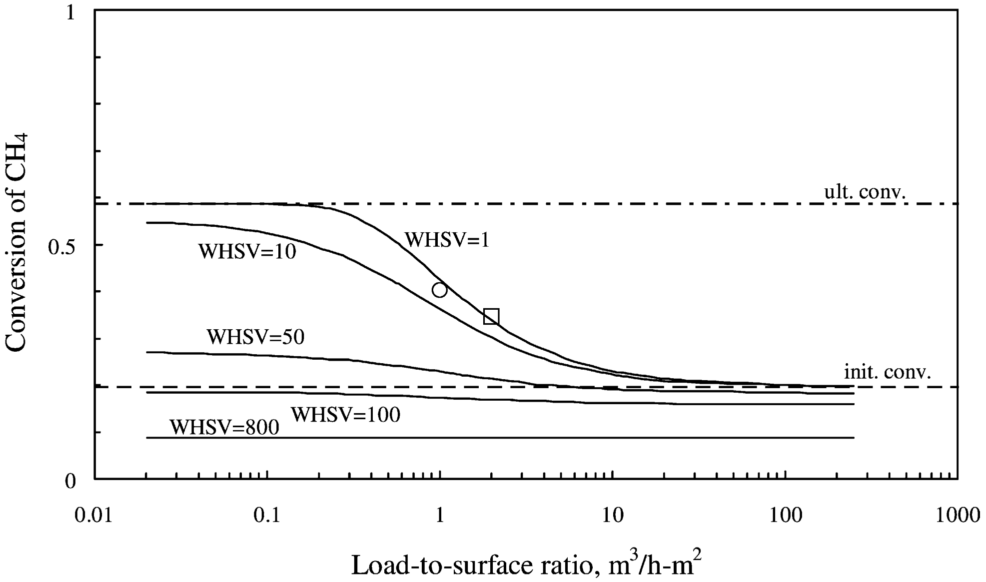

Fig. 2. Effect of load-to-surface ratio on the conversion of methane at 500 °C, 9 atm and different WHSV. The hydrogen partial pressure in permeate side was 1 atm. Experimental data were obtained at WHSV = 0.3 h^{-1} (○) and 0.6 h^{-1}(□).

obtained in conventional FBR without the use of palladium membrane. The experimental results showed good agreement with the calculation data at load-to-surface ratio of 1 and 2 $m^3/h\,m^2$ and WHSV $< 1\,h^{-1}$.

4.2. Effect of reaction pressure

Increasing the reaction pressure, and thus the pressure difference across the membrane, can significantly increase the hydrogen permeation flux of palladium membrane [6]. Therefore, the conversion of methane increased as the reforming reaction was operated at higher reaction pressure. According to the thermodynamic equilibrium, the initial equilibrium conversion, as conducted in conventional FBR without Pd membrane tube, decreases with increasing reaction pressure. As shown in Fig. 3, however, the ultimate equilibrium conversion increased from 58 up to 86% as the reaction pressure was increased from 9 to 20 atm. The experimental data also showed a conversion greater than 80% could be achieved in the palladium membrane reactor at temperature of 500 °C. Conventionally, this high conversion is usually obtained at temperatures higher than 800 °C.

When load-to-surface is greater than 10 $m^3/h\,m^2$, the conversion is approaching the thermodynamic equilibrium one due to inadequate hydrogen removal from the reaction system. The conversion obtained at reaction pressure of 20 atm was found lower than that of 9 atm. In this case, the membrane reactor approaches the traditional one so that the pressure effect is similar to the one obtained in a traditional system, i.e. methane conversion is depressed.

4.3. Achievement of hydrogen permeation flux and recovery yield

The recovery yield of hydrogen is significantly affected by the load-to-surface ratio as experimentally observed in our previous paper [11]. From the results of simulation, the recovery yield decreased with increasing load-to-surface ratio due to the rise of inlet flow rate of methane. As shown in Fig. 4, the recovery yield reaches a saturation level as load-to-surface ratio is less than 0.2 $m^3/h\,m^2$. On the other hand, the recovery yield approaches zero as load-to-surface ratio is greater than 50 $m^3/h\,m^2$. Raising the reaction pressure will increase the recovery yield of hydrogen.

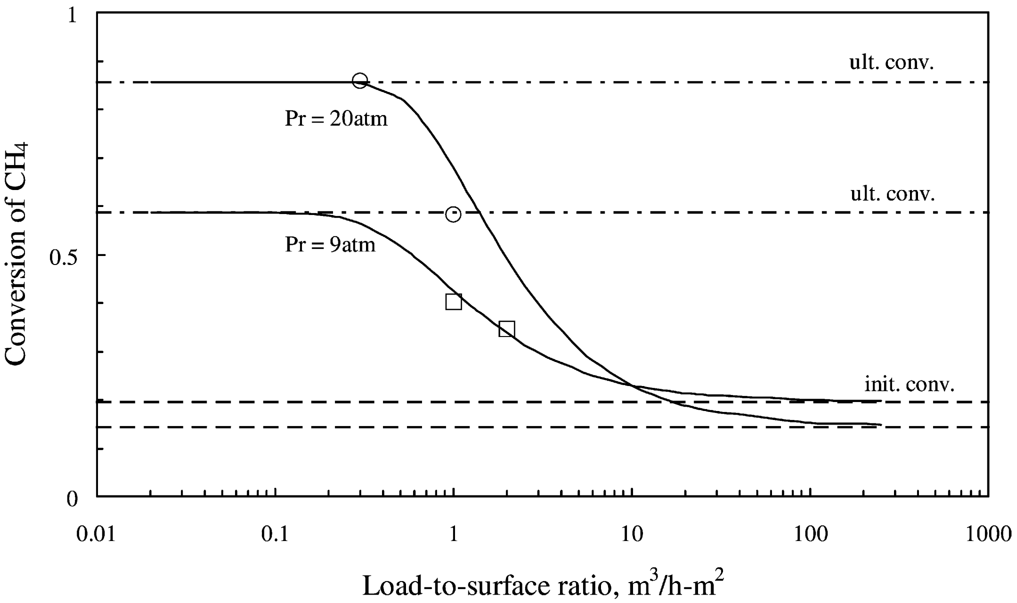

Fig. 3. Conversion of methane influenced by reaction pressure at 500 °C. The hydrogen partial pressure in permeate side was 1 atm. Simulated curves were calculated at WHSV $= 1\,h^{-1}$. Experimental data were obtained at WHSV $\leq 1\,h^{-1}$, reaction pressure = 20 atm (○) and 9 atm (□).

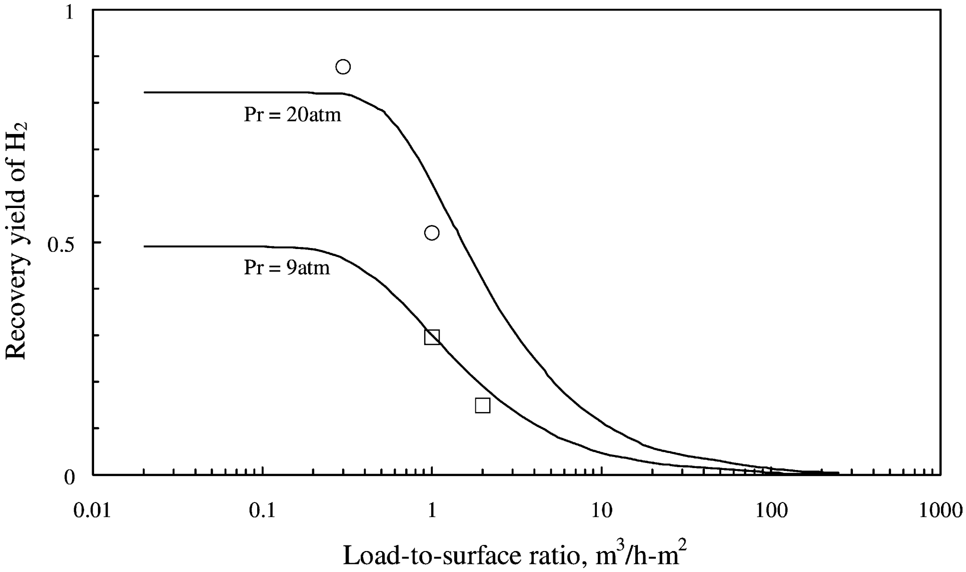

Fig. 4. Recovery yield of hydrogen influenced by reaction pressure at 500 °C. The operating conditions were the same as in Fig. 3.

At load-to-surface ratio below 0.2 $m^3/h\,m^2$, the recovery yield could be enhanced from near 50% up to above 80% as the reaction pressure increased from 9 to 20 atm. When load-to-surface ratio was greater than 50 $m^3/h\,m^2$, obvious effect of reaction pressure was not found probably due to the shortage of membrane surface and thus the conversion of methane. The dependence of recovery yield on load-to-surface ratio is similar to that of methane conversion as shown in Fig. 3.

The permeation flux showed different dependence on the load-to-surface ratio. In Fig. 5, the increase of permeation flux is observed with increasing load-to-surface ratio. A saturation level is reached, as the load-to-surface ratio is more than 20 $m^3/h\,m^2$. The higher the reaction pressure, the larger permeation flux was obtained. At load-to-surface ratio above 20 $m^3/h\,m^2$, the permeation flux could be increased from near 2 to 5 $m^3/m^2\,h$ as the reaction pressure increased from 9 to 20 atm. Because the permeation flux shows contrary dependence on load-to-surface ratio to the recovery yield, a compromise of permeation flux and recovery yield should be made to optimize these two output values. A balance exists at load-to-surface ratio around 1 $m^3/h\,m^2$ as comparing the results from Figs. 4 and 5. A recovery yield of 70% and permeation flux of 2.5 $m^3/m^2\,h$ could be obtained at reaction pressure of 20 atm.

4.4. Effect of hydrogen partial pressure in permeate side

According to the Sieverts's law, reducing the partial pressure of hydrogen in permeate side will increase the hydrogen flux. Therefore, higher conversion of methane could be obtained. As shown in Fig. 6, the conversion increased with decreasing permeate hydrogen partial pressure. When the partial pressure reduced to 0.4 atm, the calculated conversion could go up to 98%, equivalent to its ultimate equilibrium conversion. However, the experimental data showed big discrepancy from the simulation result. The larger deviation of experimental data from simulation results was found when the permeate hydrogen partial pressure became lower. As shown in Fig. 7, there exists an inversely linear correlation between the deviation and the hydrogen partial pressure. Reducing the permeate hydrogen partial pressure, the discrepancy increased. The same trend holds at various operating conditions of WHSV and load-to-surface ratio. Shu et al. [12] observed similar purge effect on the discrepancy between predicted and experimental results. However, the exact explanation of this discrepancy still needed further

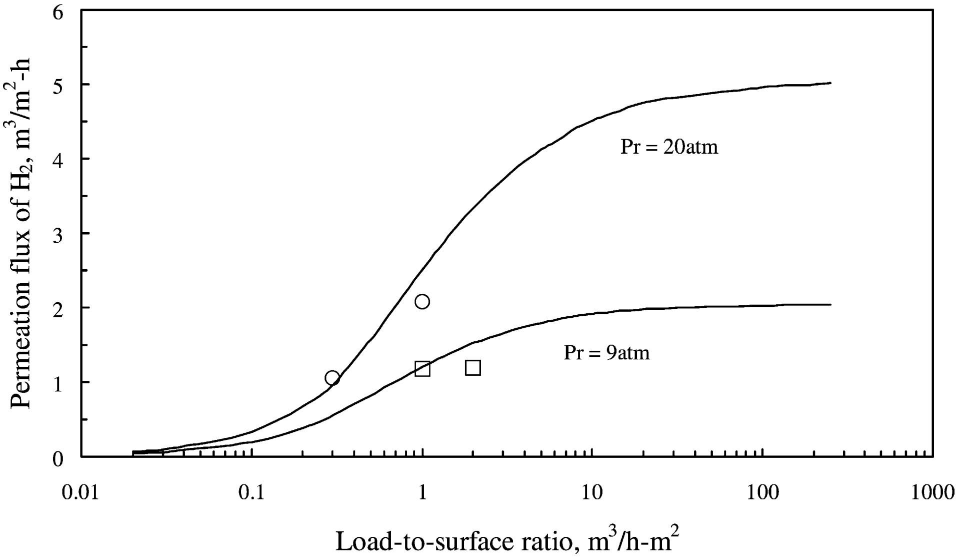

Fig. 5. Permeation flux of hydrogen influenced by reaction pressure at 500 °C. The operating conditions were the same as in Fig. 3.

investigation in both theoretical and experimental aspects.

In practical speaking, the pure hydrogen is needed for industrial purpose or as a fuel for fuel cell system. The use of sweeping gas will be limited in practical application although it can lead to higher conversion of methane.

4.5. Effect of reaction temperature

The experimental results showed that the conversion of methane obviously increased near four times the initial equilibrium conversion at temperature range from 400 to 500 °C (Fig. 8), when palladium membrane was used to incipiently remove the produced

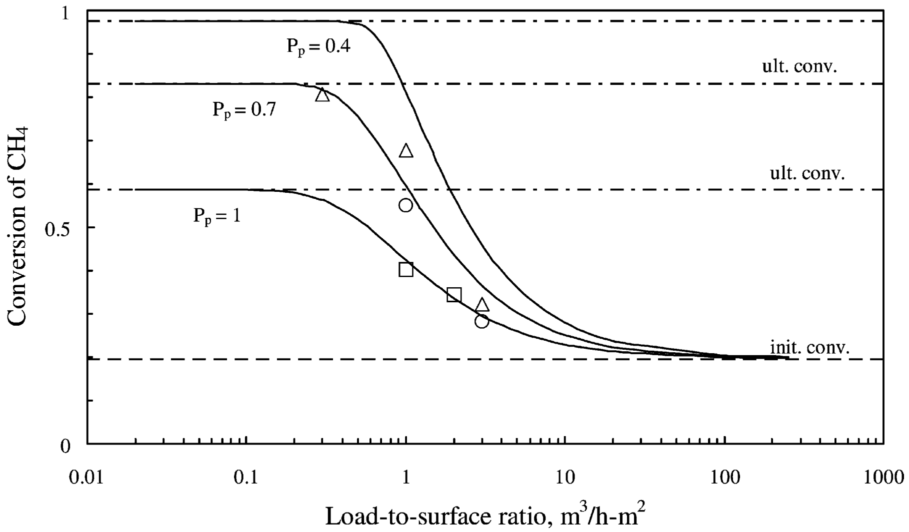

Fig. 6. Conversion of methane influenced by hydrogen partial pressure in permeate side at 500 °C and 9 atm. Experimental data were obtained at WHSV $\leq 3\,h^{-1}$, hydrogen partial pressure in permeate side = 1 atm (□), 0.7 atm (○) and 0.4 atm (△).

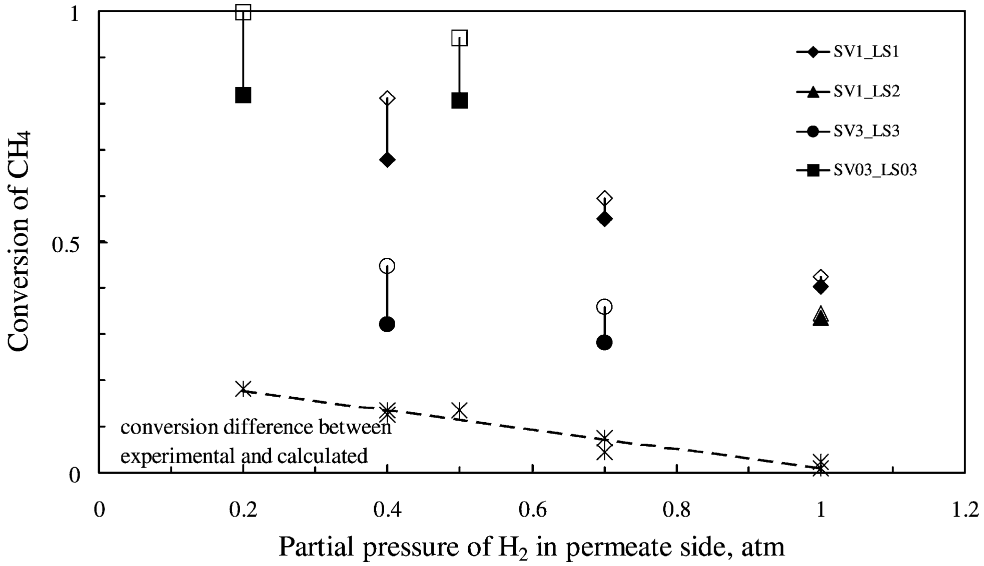

Fig. 7. Deviation of measured conversion of methane from calculated results depending on hydrogen partial pressure in permeate side at various operating conditions. Open symbols denote calculated results, solid symbols for experimental data.

hydrogen. Even at temperature as low as 400 °C, the conversion could be enhanced from 8% (initial equilibrium conversion) to 34% with load-to-surface ratio of 1 m^3/h m^2 and permeate hydrogen partial pressure of 0.3 atm. The conversion was further increased from 19% (initial equilibrium conversion) up to 65% at 500 °C. This had successfully demonstrated the achievement of high conversion at low temperatures

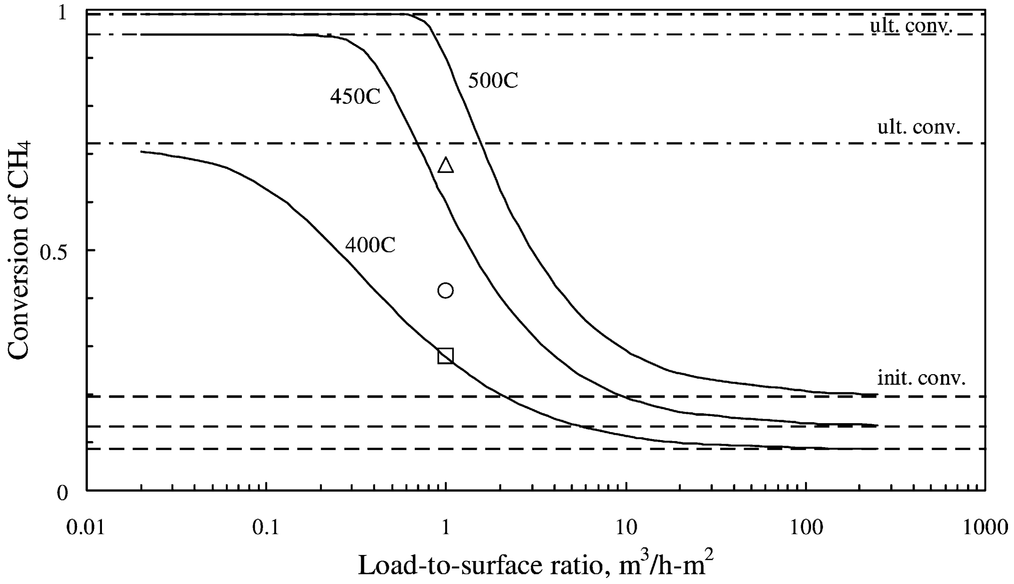

Fig. 8. Conversion of methane affected by reaction temperature at 9 atm. The hydrogen partial pressure in permeate side was 0.3 atm. Experimental data were obtained at 500 °C (△), 450 °C (○) and 400 °C (□).

Table 3
Yield of CO observed from experimental results at 500 °C and different WHSV and load-to-surface ratio[a]

Reaction pressure (atm)	WHSV (h^{-1})	Load-to-surface ratio ($m^3/h\,m^2$)	Conversion of CH_4	Yield of CO
20	3	3	0.2542	0.0037
	1	1	0.5825	0.0213
	0.3	0.3	0.8583	0.0059
9	0.6	2	0.3450	0.0144
	0.3	1	0.4025	0.0164

[a] The hydrogen partial pressure in permeate side was 1 atm.

by using palladium membrane reactor. The discrepancy between experimental and simulated results was found due to operation at reducing hydrogen partial pressure in the permeate side.

4.6. Reducing yield of CO in Pd membrane reactor (PMR)

In addition to displacing the thermodynamic equilibrium, the products profile of methane steam reforming could be also changed by using palladium membrane reactor. As shown in Table 3, the yield of carbon monoxide is always measured below 2% at reaction pressure of either 20 or 9 atm. Even at the conversion of 85%, only trace carbon monoxide (~0.6%) was produced. Fig. 9 further shows the composition profile from simulation in the retentate side along the axial direction of palladium membrane tube. Trace carbon monoxide was produced because of the removal of hydrogen through the membrane. On the other hand, the carbon dioxide was produced as the major carbon-containing product. The composition excluded water in the retentate side exited from the membrane reactor is shown in Table 4. Good agreement was found from the comparison of experimental and calculated results. These results, therefore, indicated that the intermediate product, CO, was almost completely consumed in the membrane reactor as the methane steam reforming proceeded.

In conventional FBR, the product distribution could be determined by use of the thermodynamic equilibrium constants of the two independent reactions (1) and (3). The yield of carbon monoxide in conventional reactor is much higher than from the membrane reactor. Fig. 10 compares the yield of CO and CO_2 obtained in palladium membrane reactor and conventional FBR at the same conversion of methane. According to the results of thermodynamic calculation, when the conversion is above 70%, the yield of CO is greater than CO_2 in conventional FBR. Therefore, a secondary shift reactor is needed to improve the

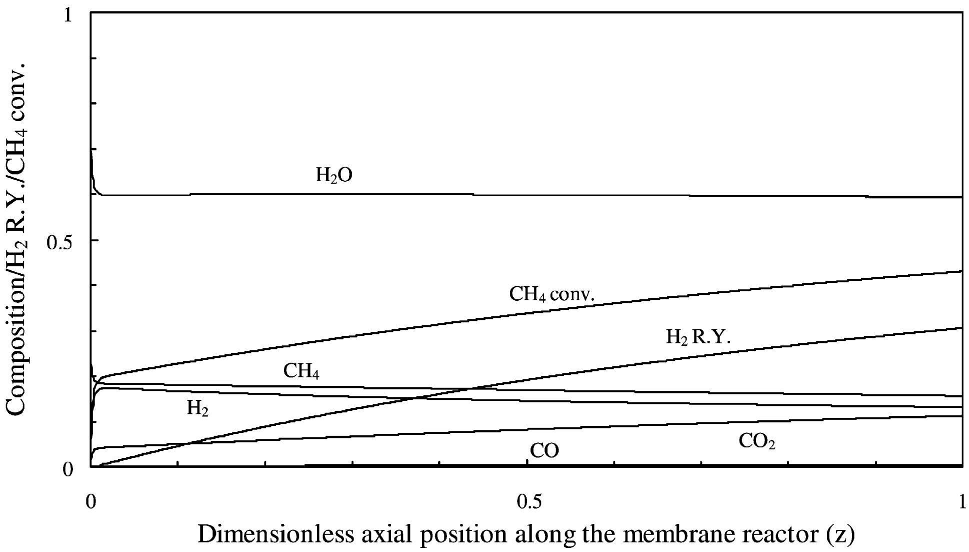

Fig. 9. The profile of each composition in the retentate side along the axial direction in PMR at reaction pressure: 9 atm, hydrogen partial pressure in permeate side: 1 atm, load-to-surface ratio: $1\,m^3/h\,m^2$ and WHSV: $0.3\,h^{-1}$.

Table 4
Comparison of experimental and calculated results of methane steam reforming at 500 °C and 9 atm[a]

	Conversion of CH_4	H_2 R.Y.	H_2 flux (m^3/m^2 h)	Composition excluded H_2O in retentate			
				CH_4	H_2	CO_2	CO
Experimental	0.4025	0.295	1.18	0.3828	0.3658	0.2411	0.0102
Calculated	0.4300	0.3058	1.20	0.3853	0.3240	0.2784	0.0123

[a] WHSV = 0.3 h^{-1}, load-to-surface ratio = 1 m^3/h m^2. The hydrogen partial pressure in permeate side was 1 atm. No sweeping gas was used in experiments to keep hydrogen partial pressure at 1 atm in the permeate side.

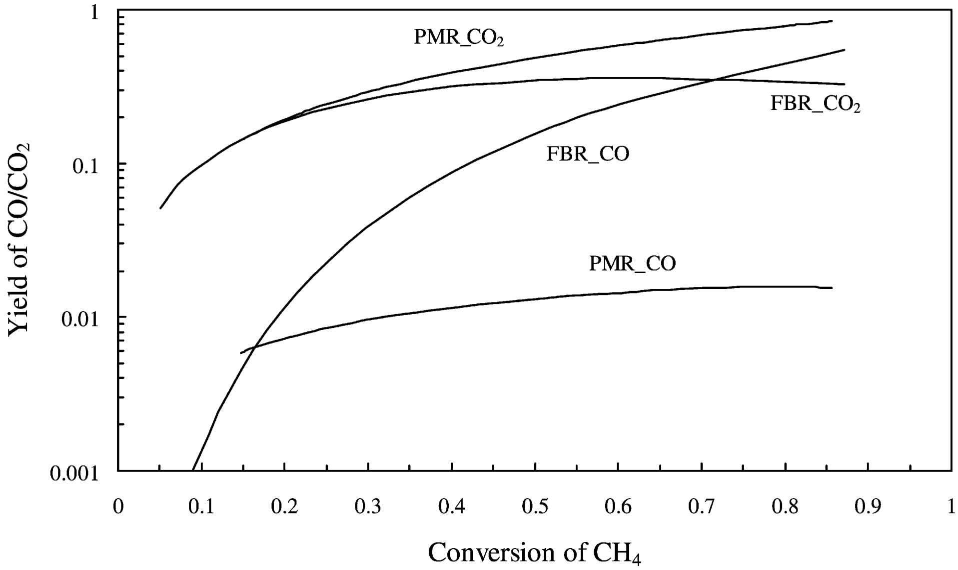

Fig. 10. Comparison of yield of CO and CO_2 at various conversion of methane between the PMR and conventional FBR. Operating conditions for calculation: PMR at 500 °C, 20 atm and load-to-surface ratio = 0.02–250 m^3/h m^2, FBR at 9 atm and reaction temperature = 350–800 °C.

hydrogen production. In membrane reactor, the yield of CO is very low (<2%) even at the conversion higher than 80%. At the same level of conversion, a much higher yield of CO (>50%) exists in the conventional FBR. That means the production of CO is obviously depressed by using palladium membrane reactor. This unique feature will lead the palladium membrane reactor to a more efficient reformer to generate pure hydrogen for application in polymer membrane or alkaline electrolyte fuel cell system.

5. Conclusion

The reaction behavior of methane steam reforming in a palladium membrane reactor was well simulated by the mathematical model based on the kinetic rates involving both reforming and shift reactions. The simulation results showed that the production of intermediate product CO was significantly reduced, due to the incipient removal of hydrogen through the membrane. When the conversion of methane is maintained at a level of 80%, only small yield of CO (<2%) is found in membrane reactor. In contrast, the yield of CO in conventional FBR is more than 50%. Decreasing the yield of CO and, thus, increasing the yield of CO_2 will result in the increase of hydrogen production. Therefore, high production of hydrogen can be achieved in only one-step operation by using membrane reactor instead of the two-step conversion as done in conventional process. High recovery yield of pure hydrogen is thus obtained without the need of extra purification facilities.

The conversion of methane is determined by the load-to-surface ratio and WHSV of methane. The lower the load-to-surface ratio or WHSV, the higher the conversion of methane. When WHSV is below $3\,h^{-1}$, the conversion reaches its equilibrium status and cannot be enhanced by reducing the WHSV. In this case, the conversion approaches the ultimate equilibrium one, as load-to-surface ratio is less than $0.2\,m^3/h\,m^2$. Increasing reaction pressure results in the increase of conversion. A 86% conversion could be achieved at 500 °C as the reaction conducted at the pressure of 20 atm. The recovery yield of hydrogen decreased with increasing load-to-surface ratio. In contrast, the permeation flux increased. They seem to be balanced at load-to-surface ratio around $1\,m^3/h\,m^2$. At reaction pressure of 20 atm, a recovery yield of 70% and permeation flux of $2.5\,m^3/m^2\,h$ could be obtained.

With the features of very low CO production, high hydrogen yield and internal purification of hydrogen, the palladium membrane reactor is potentially considered as a more efficient fuel processor to provide pure hydrogen, from methane or other hydrocarbons, for polymer membrane or alkaline electrolyte fuel cell system.

Acknowledgements

The authors want to express their thanks to CTCI Foundation for financial support of this work.

References

[1] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Appl. Catal. A 119 (1994) 305.
[2] J.R. Rostrup-Nielsen, Catalysis: Science and Technology, vol. 5, 1984, Chapter 1, p. 1.
[3] J. Shu, B.P.A. Grandjean, A. van Neste, S. Kaliaguine, Can. J. Chem. Eng. 69 (1991) 1036.
[4] E. Kikuchi, Catal. Today 25 (1995) 333.
[5] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Appl. Catal. 67 (1991) 223.
[6] Y.M. Lin, G.L. Lee, M.H. Rei, Catal. Today 44 (1998) 343.
[7] S.I. Prokopiev, Y.I. Aristov, V.N. Parmon, N. Giordano, Int. J. Hydrogen Energy 17 (1992) 275.
[8] Y.M. Lin, M.H. Rei, in: Proceedings of the Fifth International Conference on Inorganic Membranes, Nagoya, Japan, June 22, 1998, p. 600.
[9] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.R. Flannery, Numerical Recipes in C. The Art of Scientific Computing, 2nd ed., Cambridge University Press, Cambridge, 1992, p. 714.
[10] P.P. Mardilovich, Y. She, M.H. Rei, Y.H. Ma, AIChE J. 44 (1998) 310.
[11] Y.M. Lin, M.H. Rei, Int. J. Hydrogen Energy 25 (2000) 211.
[12] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Catal. Today 25 (1995) 327.